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Third Quarterly Report

RESEARCH & DEVELOPMENT
ON
ELECTRODEPOSITED INORGANIC SEPARATORS

15 October 1965 - 15 January 1966

Contract No. NAS5-9168

Prepared by
General Electric Company
Research and Development Center
Schenectady, New York

Prepared for
NASA
Goddard Space Flight Center
Greenbelt, Maryland

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SUMMARY

The objective of this program is to evaluate the use of thin electro-deposited films of calcium and magnesium hydroxides as separators in silver-cadmium cells. Potential gains to be made with the successful development of these separators are increased thermal stability at elevated temperature and a reduction in silver migration.

During the third quarter, work was continued on determining the effect of deposition process parameters on the rate of film deposition and on the uniformity and adherence of the resulting films. Electrodes showing the best films were assembled into test cells to determine charge-discharge characteristics and a preliminary estimate of silver migration during cycling. All of the work was done with calcium hydroxide films, since previous work showed these films to be more adherent than the magnesium hydroxide films.

The variables investigated were the state of charge of electrode prior to deposition of the films and the effect of the presence or absence of electrolytes in the electrode pores prior to starting the coating process. The electrode states of charge investigated were: (1) Uncharged in the as-received conditions; (2) Cycled-Discharged, charged at 200 ma for 6 hours, discharged at 250 ma for 4 hours and then shorted overnight to the counter cadmium electrode; (3) Cycled-Charged, cycled as in (2) and then charged again at 200 ma for 6 hours, (4) Reverse Coated, electrodes of types (1) or (2) above were charged in the coating electrolyte (calcium acetate) at a current density of 93 ma/cm² for 10 to 20 minutes prior to reversing polarity for depositing the calcium hydroxide. The other parameter investigated was the effect of the presence of 31% by weight potassium hydroxide in the electrode pores prior to coating versus the presence of distilled water or drying the electrode, containing distilled water, in air for several hours at 145°C. These coatings were applied at a current density of 93 ma/cm² using an electrolyte containing 70 g/l of calcium acetate. Most of coatings were made with a deposition time of 20 minutes with a few runs lasting 15 and 30 minutes.

The most uniform and adherent films were obtained with electrodes that were Cycled-Discharged, Cycle-Charged, or Reverse Coated-Charged as described above. Electrodes in the Cycle-Charged state yielded the most uniform coatings thicknesses; the electrodes in the Uncharged state yielded the poorest coatings. The electrodes which were air dried at 145°C yielded the most uniform coatings and the electrodes with potassium hydroxide in the pores yielded poor or no coatings at all. Electrodes having the best films were assembled into test cells at the end of the quarter. Charge and discharge characteristics of these electrodes will be reported in the next quarterly report.

The effect of the sterilization procedure on two uncoated silver electrodes was also investigated. The electrodes were sterilized in 31% by weight potassium hydroxide at 145°C for 40 hours. These electrodes were then given five charge-discharge cycles (charge rate 100 ma and discharge rate 200 ma) against two counter cadmium electrodes. The maximum capacity developed on any cycle was 275 ma. hrs., approximately 25% of the nominal capacity. The cause for this inability to develop normal capacity is not known. Further experiments are planned to elucidate the phenomenon.

The experimental work effort was decreased below the normal effort during this quarter because of year-end vacation schedules and jury duty service on the part of Mr. E. L. Roberts, who has been carrying out the experimental studies.

1.0 INTRODUCTION

This report covers the work done during the third quarter of a 12-month program to evaluate the use of thin electrodeposited films of calcium and magnesium hydroxide as separators in silver-cadmium cells. The potential advantages to be gained in using these separators are an increase in chemical stability of the cell separators at elevated temperature and a reduction in silver migration.

The objective of the program is twofold: first, to determine the effect of process parameters on the thickness, porosity and adherence of the films on representative silver and cadmium electrodes, and second, to evaluate the performance of these films in single cells in terms of electrolyte retention, internal cell resistance, charge-discharge characteristics, control of silver transport, and stability at elevated temperatures.

During the third quarter, process studies were continued with the aim of determining the best deposition conditions for obtaining uniform and adherent coatings along with a minimum increase in the resistance contributed by the film forming in the pores of the electrode. Principal parameters investigated were the state of the electrode prior to coating, uncharged in the as received condition, cycled once by charging at 200 ma for 6 hours and discharged at 50 ma, cycled once as above and then fully charged in potassium hydroxide, or partially charged in the calcium acetate bath used for coating. In addition, the effect of the presence of potassium hydroxide, and water in the electrode pores versus a water rinsed electrode dried in air at 145°C for several hours was also determined. All of these tests were made at a constant current density of 600 ma/in.² and a coating electrolyte concentration of 70 g/l of calcium acetate. Coating time was held essentially constant at 20 minutes for all of these tests.

In general, the most complete coverage of electrodes and most adherent films were obtained with electrodes that had been cycled once or were in the charged or partially charged state. The best coatings were obtained with those electrodes that were rinsed with distilled water and then dried at 145°C for several hours prior to coating. Electrodes which had 31% by wt. potassium hydroxide solution in the pores prior to coating, yield partially coated electrodes and, in some cases, no coating at all.

Some of the electrodes from these experiments have been assembled into test cells and are being cycled to determine charge-discharge characteristics.

In addition to the coating experiments, the effect of subjecting uncoated silver electrodes to the sterilization procedure used on the coated silver electrodes during the previous quarter was investigated. These results indicate that uncoated electrodes lose their ability to develop their nominal capacity after sterilization at 145°C for 40 hours in 31% by wt. potassium hydroxide solutions. Further experiments are being performed to determine the cause of this phenomena.

2.0 DISCUSSION OF EXPERIMENTAL RESULTS

2.1 Process Parameter Studies

Previous work has shown that the weight and thickness of films deposited on the electrode from a given solution is proportional to the number of Faradays transferred. Over the range of current densities investigated to date (200-1000 ma/in.²), the electrochemical efficiency of the process is in the range of 40 to 50%. The most reproducible results and more uniform coatings have been obtained at current densities in the range of 400 to 1000 ma/in.² (60-150 ma/cm²).

The electrode-electrolyte interface resistance measured in 31% by weight potassium hydroxide using a 1000 cps bridge, have shown more scatter than the weight and film thickness results. The resistance values of the uncharged silver electrodes as removed from the cells, show a ratio of three to one in resistance values, maximum to minimum.

Precautions were taken during this quarter to allow the electrode to soak in the potassium hydroxide solution for a period of twenty-four hours or more to insure penetration of the electrolyte into the pores before making the resistance measurements. Using this procedure, the resistance values obtained on full size silver electrodes in the as received conditions, ranged from 0.08 to 0.17 ohms; a ratio of two to one, maximum to minimum.

2.1.1 Experimental Procedure

The state of charge of the electrodes prior to coating were as follows:

1. Uncharged as removed from the YS5 (S)-4 cells.
2. Cycled-Discharged, cycled once, charged at 200 ma for 5 hours, discharged at 250 ma for four hours then shorted to the cadmium counter electrode overnight.
3. Charged, cycled once as above (2) and then charged again at 200 ma for 5 hours.
4. Reverse Coated, electrodes of types (1) or (2) above, were partial charged in the coating electrolyte (calcium acetate) for periods of 10 to 20 min. prior to reversing the polarity and then proceeding with the deposition of calcium hydroxide.

The electrodes in one of the above conditions were pretreated by one of the following steps prior to immersion and coating in the calcium acetate electrolyte.

1. Potassium Hydroxide - the electrode was soaked in a 31% by weight solution for a period of twenty-four hours; removed from the solution and the excess alkali was sponged off with a paper towel.
2. Water - the electrode was first soaked as in item 1 above, then rinsed in distilled water until the water rinse was essentially neutral, removed from the water, and excess water was sponged off with a paper towel.

3. Dried - the electrode was treated as described in item 2 and then was dried in an air circulating oven at 145°C for a period of two hours.

The electrodes were all coated in one liter of electrolyte containing 70 g/l of calcium acetate buffered with approximately 1.0 grams of calcium hydroxide. Additional calcium hydroxide was added in 1.0 gram increments after every two to three coating runs. The current density for all runs was 600 ma/in.² (93 ma/cm²). The coating time was normally 20 minutes, with a few experiments at 15 and 30 minutes.

Following the coating step, the electrodes were rinsed with distilled water, soaked in potassium hydroxide for a period of twenty-four hours and the 1000 cps resistance measurements were made as previously described. The electrode was rinsed again in distilled water, oven dried at 145°C for one hour, weighed and remeasured for thickness.

The experimental data are summarized in the Appendix, Section 5.0.

2.1.2 Results and Conclusions

The weight gain, film thickness, and resistance changes for the coated electrodes are summarized in Table I.

The most significant points are as follows:

1. The electrodes, regardless of state charge, which were dried, produced the most uniform coats. The electrodes containing water in the pores were intermediate and poor coatings or no coating were achieved with potassium hydroxide in the pores.
2. The electrodes which had been cycled and discharged or charged, produced the most uniform coatings. Visually the ones produced from the charged electrodes were more uniform in appearance than the cycled and discharged electrodes.
3. Resistance changes are still variable. Resistance values of pre-treated coated electrodes show less increase than has been observed in the previously reported work.

2.2 Test Cells

Electrodes numbered 18, 20, 23, 25, having the best films were assembled into test cells containing one coated electrode and two sintered plaque type cadmium counter electrodes. A single layer of separator was wrapped around the coated silver electrode. The cells are of open top construction. The cell electrolyte volume is approximately 6 cc. and the cells are running in the flooded mode. A reference mercury-mercuric oxide electrode is mounted on the cell assembly and connects to the cell electrolyte via a 1/16 in. diameter port at the bottom of the cell.

These cells will be formed at a 50 ma. charge rate for one or two cycles and then cycled for a few cycles at a charge rate of 100 ma. and discharge rate

200 ma. Cell voltage during the cycle will be recorded and periodic measurements of individual electrode voltage versus the reference electrode will be made during the charge and discharge portion of the cycle. Subsequent to cycling, the cells will be disassembled, the electrodes will be checked for film resistance changes and weight changes. The electrolyte and separator will be analyzed for silver content to determine the extent of silver migration. A test cell containing an uncoated silver electrode is included in the test group as a reference for comparison.

2.3 Effect of Sterilization on Uncoated Silver Electrodes

In the previous quarter, silver electrodes coated with calcium hydroxide films were sterilized at 145°C in 31% potassium hydroxide for 40 hour periods. Charge-discharge tests made after sterilization showed variability in the charge acceptance of the electrodes. The reasons for this variability were not apparent from the experimental measurements on hand.

It was decided to determine if the sterilization procedure affected the charge acceptance of uncoated electrodes. Two uncharged silver electrodes, removed from YS 5(S)-4 "Silcad" cells were sterilized at 145°C for a period of 40 hours. The electrodes were totally immersed in a solution of 31% potassium hydroxide, contained in a Teflon beaker which in turn was sealed in a steel bomb for the sterilization. After sterilization, the electrodes were assembled into a test cell using two counter sintered plaque cadmium electrodes and given five charge-discharge cycles. The charge rate was 100 ma for 12 hours and discharge rate was 200 ma. Electrode-electrolyte interface resistance measurements using a 1000 cps bridge were made before and after sterilization, and after cycling. The results of the capacity data are given in Table II.

The significant result is the inability of these electrodes to develop full capacity as was observed for some of the coated electrodes previously. The extrapolated 1000 cps resistance values of the two electrodes were different.

	Before Sterilization <u>ohms</u>	After Cycling <u>ohms</u>
Electrode No. 1	.105	.072
Electrode No. 2	.070	.175

Although the electrodes showed a difference in final resistance values, the behavior of the electrodes, with respect to charge capacity developed, was similar. It is possible that the wire grid in the electrode structure was oxidized during the sterilization and reduced the electrical contact to the electrode. An attempt will be made to reverse charge the electrode to see if this results in an improvement of the capacity developed.

TABLE I

EFFECT OF ELECTRODE PRETREATMENT ON CALCIUM HYDROXIDE FILMS

Electrode-State and Pretreatment	No.	Resistance - ohms		Weight Gain Grams	Film Thickness mils/side	Remarks on Film Quality	
		Initial	Final				
<u>Uncharged-KOH</u>	3	.150	.080	.073	0.1	Partially Coated	
	4	.150	.043	.068	<0.1	No Coat	
	8	.111	.101	.034	<0.1	No Coat	
	12	.111	.062	.043	0.1	No Coat	
	Reverse Coating for 10 min.	2	.080	.127	.045	1.4	Coated
	H ₂ O	6	.112	.083	.105	0.4	Partially Coated
		7	.112	.053	.100	0.4	Partially Coated
		15	.092	.112	.032	---	No Coat
		16	.111	.088	.037	<0.1	No Coat
	Dried	10	.100	.110	.178	0.85	Coated
		11	.120	.090	.191	1.05	Coated
<u>Cycled-Discharged-KOH</u>	5	.043	.100	0.200	2.25	Partially Coated	
	9	.098	.061	0.164	2.55	Partially Coated	
	H ₂ O	1	.110	.068	.324	3.0	Coated
		13	.081	.119	.437	3.2	Coated
	Reverse Coating for 20 min.	19	.162	.072	-.362	0	No Coat
		20*	.100	.260	+.371	4.7	Coated
		17*	.130	.060	-.075	1.9 ⁽¹⁾	Partially Coated (1)Thickness where coated
	Dried	21	.170	0.080	.254	1.5	Coated
		22	.170	0.070	.288	1.5	Coated
	<u>Charged-H₂O</u>	23	.140	.130	.480	1.4	Coated
		24	.130	.300	.718	3.0	Coated
14		.120	.070	.295	1.8 ⁽¹⁾	Partially Coated (1)Thickness where coated	
Dried		18	.170	.175	.304	1.25	Coated
	25	.170	.175	.525	2.0	Coated	

NOTES: Electrodes - Full Size Silver 1-5/8" x 1-1/2"
 Electrolyte Concentration - 70 g/l of calcium acetate
 Coating Time - 20 minutes nominal
 Current Density - 600 ma/in.²

*Coated in a fresh volume of electrolyte after reversal.

TABLE II
CAPACITY OF UNCOATED SILVER ELECTRODES
AFTER STERILIZATION

<u>Cycle</u>	Electrode 1		Electrode 2	
	Charge ⁽¹⁾ <u>ma.hrs.</u>	- Discharge <u>ma.hrs.</u>	Charge ⁽²⁾ <u>ma.hrs.</u>	- Discharge <u>ma.hrs.</u>
1	1200	225	1200	250
2	1200	240	700*	160
3	1300	240	1200	235
4	1200	275	1200	225
5	1200	275	1200	225

*Cell shorted during charge portion of cycle. Cells charged at 100 ma, discharged at 200 ma.

- (1) Maximum voltage during charge portion of cycle 1.56
- (2) Maximum voltage during charge portion of cycle 1.69
- (3) Length of Ag⁺ voltage plateau was variable from cycle to cycle and different for the two electrodes.

3.0 PROGRAM FOR NEXT QUARTER

The process parameter studies will be complete early in the quarter. Electrodes will be coated under the best conditions to several film thicknesses. These electrodes will be evaluated in test cells under cycling conditions to determine charge-discharge characteristics and the extent of silver lost from the electrode. Cells will be modified with the best performing electrodes.

4.0 NEW TECHNOLOGY CLAUSE

There were no developments during this period that come under the "New Technology" clause of this contract.

5.0 APPENDIX

TABLE III

SUMMARY OF FILM DEPOSITION DATA FOR CALCIUM ACETATE ELECTROLYTE

Electrode-State and Pretreatment	No. Elec.	Initial		Resistance		Coating Time Min.	Initial		Final	Volts	Weight Gain Grams	Film Thickness mils./side
		Weight Grams	Thickness mils	Initial	Final		Volts	ohms				
<u>Uncharged-KOH</u>	3	6.277	28.5	.150	0.080	15	6.6		24		.073	0.1
	4	6.883	28.3	.150	0.043	15	5.8		34		.068	0.05
	8	6.900	28.8	.111	.101	20	6		42.6		.034	0.05
	12	6.622	28.5	.111	.062	20	5.5		42.8		.043	0.1
Reverse Coating for 10 min.	2			.080	.127	15	4.9		34		.045	1.35
H ₂ O	6	7.197	29.0	.112	.083	15	6.4		33		.105	0.4
	7	6.885	28.8	.112	.053	15	5.6		18		.100	0.35
	15	6.610	28.4	.092	.112	20	5.9		42.8		.032	0
	16	6.656	28.5	.111	.088	20	5.2		42.8		.037	0.05
Dried - 145°C	10	6.857	28.7	.100	.110	20	6.4		25		.178	0.85
	11	6.877	28.9	.120	.090	20	5.7		38		.191	1.05
	5	6.674	28.2	.043	0.100	20	6.4		42.8		.201	2.15
	9	6.662	28.6	.098	0.061	20	5.1		42.8		.164	2.45
<u>Cycled-Discharged-KOH</u>	1	6.817	28.5	.110	.068	20	5.4		42.6		.324	3.0
	13	6.694	28.6	.081	.119	20	5.0		42.8		.437	3.2
	21	6.599	28.6	.170	0.080	20	6.5		42.8		.254	1.5
	22	6.764	28.5	.170	0.070	20	5.9		42.6		.288	1.55
Dried - 145°C	19	6.762	28.6	.162	.072	30	4		42.9		-.362	0
	20*	6.852	28.7	.100	.260	20	6.2		42.6		+.371	4.7
	17*	6.726	28.7	.130	.060	20	5.0		42.6		-.075	*1.9
<u>Charged-H₂O</u>	23	6.656	28.6	.140	.130	20	5.6		42.9		.480	1.4
	24	6.672	28.1	.130	.300	25	4.5		42.9		.718	3.0
	14	6.655	28.5	.120	.070	20	5.0		42.6		+.295	*1.75
	18	6.738	28.5	.170	.175	20	5.4		42.9		.304	1.25
Dried - 145°C	25	6.413	28.1	.170	.175	20	4.8		42.8		.575	2.0

NOTES: Electrolyte Concentration - 70 g/l

Full Size Electrodes - 1-5/8" x 1-1/2"

*Coated in a fresh volume of electrolyte after reversal.